

# PATENT SPECIFICATION

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## DRAWINGS ATTACHED

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## (54) CONTINUOUS BULK POLYMERISATION PROCESS

(71) We, DEUTSCHE GOLD-UND SILBER-SCHNEIDANSTALT VORMALS ROESSLER, a body corporate organised under the laws of Germany, of 9, Weissfrauenstrasse Frankfurt/Main, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a continuous bulk polymerisation process.

The continuous bulk polymerisation of trioxane, optionally in conjunction with comonomers, with the aid of cationic catalysts in the absence of oxygen can be carried out in a plastics tube by introducing the polymerisation mixture into the plastics tube after substantially all the air has been displaced from it, and continuously passing the tube thus filled through a liquid bath heated to the polymerisation temperature or through a heating duct and, optionally, through a cooling bath.

In the practical application of this process, the plastics tube is formed by joining and welding together one or more lengths of plastics material, welding being carried out shortly after the tube has passed the pipe through which the polymerisation mixture is introduced into it. However, it is also possible to use a prefabricated tube which is slit open just before it passes the opening of the feed pipe and then welded together again. In either case, the tube is cut open again on completion of polymerisation and the polymer removed. The plastics tube can be re-used after renewed extrusion although this does involve an additional operation. It is also possible in this process to cut open the tube in such a way that it can be directly re-used, although it is often necessary to prepare the edges for re-welding. If in this process it is intended to seal the tube by welding, it is only possible to use weldable materials whose

resistance to temperature is of course limited (DAS 1,244,408).

The object of the present invention is to provide an alternative method for bulk polymerisation. The invention makes it possible to widen the range of tube materials which can be used for carrying out polymerisation in a manner similar to that referred to above and to improve the ability of such materials to be re-used.

The present invention provides a process for the production of a homo or copolymer by continuous bulk polymerisation in the presence of a polymerisation initiator in which a polymerisation mixture is continuously introduced by means of at least one feed unit in at least one feed zone into a continuously moving sheath after substantially all the air has been displaced from the sheath, the sheath being formed of a flexible material which lies loosely in the vicinity of the feed zone, and the sheath is thereafter guided through a zone heated to the polymerisation temperature and optionally through a cooling bath, the sheath being formed continuously from two separate webs of the flexible material which are guided together in the vicinity of the feed unit so that they lie loosely one on top of the other with the feed unit in between them, or from a single web of the flexible material which is folded along one line or along two lines in the vicinity of the feed unit so that two portions of the web lying loosely one on top of the other are formed with the feed unit in between them, and after passing the feed unit, but before reaching the zone heated to the polymerisation temperature, the open longitudinally extending edge zones of the web(s) lying one on top of the other are brought together and bent upwards by guide means to form the sheath acting as a liquid-tight polymerisation vessel, in such a way that the sheath either takes the form of two troughs inserted one inside the other, the polymerisation mixture filling the bottoms of the

lower trough whilst the side walls of both troughs run parallel to one another above the polymerisation mixture and are bent upwards or takes the form of a slit tubular structure with parallel edges, the edge(s) of the tubular structure which extend beyond the polymerisation mixture being bent upwards.

In the process according to the invention, therefore, the sheath acting as a liquid-tight vessel is formed simply by shaping the flexible material along its edges without any need for a permanent closure such as by welding, sewing, bonding or clipping. The expense that these operations involve in terms of apparatus is thus eliminated and in addition the range of flexible materials that can be used is considerably widened because the material no longer require the properties needed for conventional sealing methods. This is of particular advantage by virtue of the relatively wide range of variations which it affords in regard to the temperature programme both during polymerisation and optionally during additional heating or cooling stages. Since the web or webs is/are not permanently sealed, there are no difficulties in re-using the material. For example, the material can be unwound from a roll at one end of the polymerisation apparatus, joined together to form the sheath and, after leaving the polymerisation apparatus, can readily be rewound on to a roll. This winding machine simultaneously provides for the passage of the sheath through the polymerisation zone and optionally through additional temperature zones. The material is then immediately available for re-use. Instead of unwinding and rewinding the webs of flexible material, they may also be guided in the form of an endless band. Another particular advantage is that no separate release means are required for opening and separating the sheath from the polymerised material. It is of course also possible to leave the sheath as it stands and to use it as a packaging material.

One surprising and unpredictable advantage of the process according to the invention is that a liquid-tight tubular structure may be formed, even with continuous movement, simply by bending the edge zones of the web or web portions of flexible material upwards, i.e. without applying a permanent seal. Leaks and, in the case of thin tubular materials, cracks would have been expected to be formed due both to the differing tensile stresses to which the various sections of material are subjected over the fairly considerable length of the polymerisation zone and to the transition of the contents of the sheath from the liquid to the solid state.

The invention also provides an apparatus for carrying out a bulk polymerisation process comprising means for forming one or two webs of flexible material into a continuously moving sheath, feed means for introducing a

polymerisation mixture into the sheath, a zone capable of being heated to the polymerisation temperature and means for guiding the sheath therethrough, the forming and guiding means either being adapted to form after insertion of the polymerisation mixture by the feed means a single web into a slit tubular structure with parallel edges, the edges of the slit being bent upwards, or two webs into two troughs inserted one inside the other, the edges of which are brought together and bent upwards. Preferably the apparatus also includes means for discharging polymer formed from the sheath.

The invention is described more fully with reference to the accompanying drawings, in which:—

Figures 1a, 1b and 1c show diagrammatically in cross-sectional profile the formation of the sheath using a liquid bath;

Figure 2 is a diagrammatic side elevation of one example of the apparatus as a whole;

Figure 3 is a perspective view of one zone in the apparatus of Figure 2;

Figure 4 shows examples of forming means for the flexible webs;

Figures 5 and 6 show alternative guide means for use in the cooling bath of Example 1; and

Figures 7 and 8 show diagrammatically the apparatus used in Example 2.

Figure 1a shows the simultaneous upward bending of the longitudinally extending edge zones of the webs of flexible material in cases where two separate webs are used. A polymerisable mixture 7 is accommodated between an upper web 1 and a lower web 2. The two webs form two trough-like containers inserted one inside the other. A U-form cross-sectional profile is formed. Edge zones 5 of the webs of flexible material are bent upwards together and form the side walls of the troughs, these side walls being fitted tightly on to one another so that, by bending at 6, the webs of flexible material are completely closed to form a liquid-tight sheath. On the one hand, this prevents the polymerisation mixture from running out, whilst on the other hand the contents of the sheath are separated for example from the liquid of the tempering bath and protected from other harmful outside influences. The reference 8 denotes the liquid in a liquid bath from which the edge zones 5 project snorkel-fashion.

Figure 1b illustrates upward bending in cases where only one web of flexible material is used being folded along one line (in the case illustrated this is the centre line of the web of flexible material), whilst Figure 1c shows the case where although once again only a single web is used, it is folded along two lines. In Figure 1c, these lines are in the form of two lines parallel to the centre line of the sheet of flexible material. In Figures 1b and 1c, edge zones 5 are each bent at 6

along the edges of the slit in the tubular structure where they are fitted together and bent upwards so that they project from liquid bath 8. In this way, an L-shaped cross-sectional profile is formed in Figure 1b, and an inverted-T cross-sectional profile in Figure 1c. A suction means 19 for example may also be provided above those points where the edge zones of the sheets of flexible material project from the liquid bath.

There is no need for the profiles shown in Figures 1a to 1c to be symmetrical. For example, the inverted-T (Fig. 1c) may also be of such a configuration that the vertical stem is situated outside the centre line as already shown in the Figure. Other profiles with thickness-to-width ratios different from those shown in Figures 1a to 1c are, of course, also possible. The layer thickness of the mixture to be polymerised is variable and polymerisation can also be carried out in the form of a relatively thick layer.

Figure 2 is a diagrammatic side elevation of one example of the apparatus as a whole. Webs 1 and 2 are unwound from rolls 14 and guided together in the vicinity of feed unit 15 so that the two webs lie directly one on top of the other, displacing the air between them. The edge zones are bent upwards together and hence a liquid-tight sheath is formed in zone 16 by means of guide means (not shown). In this zone, the sheath is steeply inclined in the direction in which it is travelling, so that while it is being filled with the liquid polymerisation mixture almost all the air is displaced from it. As it continues its travel, the sheet of material is then switched to a horizontal course. In cases where a liquid bath is used, edge zones 5 bent upwards together project beyond the liquid level. The guide means which can be arranged over the entire length of trough 9 extend up to zone 17. In this zone, the sheath follows an upward path, especially in cases where a liquid bath is used, so that the sheets of flexible material are converted back into their original flat form, the polymer being simultaneously removed. Guiding the sheath in this way in the form of a trough can of course be repeated several times for example in order to carry the sheets of flexible material through further temperature zones and process stages. Known release agents and release mechanisms may of course also be used for converting the sheets back into their original flat form, although in most cases this is not necessary. The sheets are then wound on to rolls 18. In cases where an endless band is used, sheets 1 and 2 are delivered for example over rolls 18 back to rolls 14. Before entering the zone 17, the sheath can of course be carried through further temperature zones (not shown) such as for example tempering zones or cooling zones or other process stages (for example extraction stages). In cases where only one

web of flexible material is used, the pairs of rolls 14 and 18 are replaced by individual rolls. In this case, before entering zone 16, the web of material is folded either along its centre line or along lines parallel to the centre line by means of forming devices.

Figure 3 is a perspective view of zone 16 in Figure 2. The height of the edge zones 5 has to be such that in cases where a liquid bath is used, they project beyond its liquid level. If the sheath is steeply inclined in the vicinity of the feed zone and guided horizontally in the polymerisation zone, the edge zones 5 must be folded upwards far enough to project beyond the filling level at the feed unit to prevent the liquid polymerisation mixture overflowing.

The edge zones are bent upwards by suitable mechanical forming or shaping means, for example by guide plates and/or guide rods and/or guide rollers. Examples of forming agents such as these and their arrangement are shown in Figure 4. As shown in this figure, a sheath is guided through a long trough 9 containing a liquid 8; instead of being guided through a liquid bath, the sheath could also be guided through an air bath. In addition, the polymerisation temperature can be adjusted for example by spraying on a liquid through spray nozzles 10. However, polymerisation can also be carried out in the absence of outer cooling and in the absence of any special measures to dissipate the heat of polymerisation. In one of the cases illustrated, forming is effected by guide rods 11 which could equally well be in the form of rollers. In the other case, forming is effected by guide plates 12. Combinations of these means are also possible. The underneath of the sheath is supported by a perforated plate 13 which could equally well be replaced by rollers optionally arranged at a given distance apart. Corresponding means may also be provided above the sheath. In cases where only one web of a flexible material folded along its centre line is used, the guide means 11 and 12 may be replaced by a simple stop or abutment along the folded side of the web of flexible material. Since the webs of material are highly flexible, the means by which they are formed can be of suitably light weight design. Especially in cases where a liquid bath is used, there is also no need for them to be arranged over the entire length of the apparatus. In many cases, it is sufficient to provide them at only a few points. In addition, the guide means may also be used for temperature control for example by having them separately cooled or heated or by making them tubular and having a cooling liquid, for example, flowing through them.

While the polymerisable mixture is still plastic, the layer thickness of the mixture can be adjusted as required for example by

two rollers. In this way, it is also possible to control or prevent harmful overheating.

5 The tubular sheath is filled with the polymerisable mixture by such means as for example tubes, flexible tubes, chutes etc. which are inserted between the webs of flexible material and which extend up to the vicinity of the edge zones which have been bent upwards together. Other feed units can  
10 of course also be arranged behind the first feed unit, each of them being introduced through the edge zones. Substantially all the air is displaced by virtue of the fact that the webs or web portions of flexible material lie  
15 loosely one on top of the other in the vicinity of the first feed zone, above all immediately before it, so that there is no need to use an inert gas during filling. Nevertheless, an inert gas may additionally be used.

20 The polymerisation mixture flows into the sheath which at this point is preferably following an inclined course, and fills it. Since the sheath consists of a flexible material, it can assume almost any cross-section or may be  
25 converted into any cross-section by suitable means. In cases where a liquid bath is used, expansion or inflation can occur due to the difference in density between the liquid bath and the filled sheath, especially before polymerisation. In this case, the sheath has to be  
30 kept below the level of the liquid bath by such means as for example guide plates. These guide plates may also be used for forming the polymer to be prepared. Dissipation  
35 of the heat of polymerisation is promoted in cases where the filled sheath assumes a flat substantially rectangular cross-section.

Conversion of the sheet of flexible material into a tubular sheath can be made even easier  
40 by using an agent which increases the adhesion of the edge zones, for example the edge zones may be completely or partly coated with a soft adhesive. In some cases, the polymerisation mixture itself may act as adhesive, as is  
45 often the case with solutions of polymers, for example in monomers. Electrostatic charging may be used for the same purpose, especially in cases where an air bath is used. Suitable flexible materials for the sheath include flexible  
50 non-metallic materials which are not dimensionally stable, in other words materials which in the absence of any additional aids are unable to retain any specific permanent shape. When converted with aids for example into  
55 the form of a tube of circular cross-section, they collapse following removal of the aids to form a flat tube. Naturally, the flexible material should be temperature resistant and chemically inert under the conditions under  
60 which the process is carried out. For example, any stretched or unstretched films may be used providing they are inert under the polymerisation conditions and do not adhere to the polymer. Examples of suitable film  
65 materials include polyalkylenes such as poly-

ethylene, polypropylene, polyterephthalate, cellulose esters and ethers, polyamides, polyurethanes, silicones, fluorine-containing plastics, reinforced films, for example those  
70 based on glass-fibre-reinforced polytetrafluoroethylene, also composite films or lacquers films, non-weldable films, for example cellulose hydrate/polyethylene composite films, cellulose hydrate films with a  
75 lacquered coating, plastics-coated or impregnated papers, and lacquered papers. By virtue of their outstanding tensile strength, coated fabrics or webs, for example silicone-coated cotton fabrics and polyurethane-coated polyester fabrics, and metal-coated fabrics, are  
80 also particularly suitable. The wall thickness of the flexible material is generally between about 0.03 and about 2.0 mm., although wall thicknesses outside this range are also possible.  
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In cases where the polymer adheres to the sheath material, it is possible to prevent this by coating the sheath beforehand with a release agent or lubricant (for example silicone oil). This can be done for example by  
90 spraying.

In view both of the relatively long service life and of the limited degree of wear, it is best to use a relatively thick and fairly high quality material for the sheath because in  
95 most cases a material of this kind can withstand greater mechanical loads and can be removed more quickly.

In cases where two webs of flexible material (for example as shown in Figure 1a) are used,  
100 it is of course possible for the two webs to differ in thickness. Similarly, they can also consist of different materials.

It is also possible to use a double web, i.e. two webs lying one on top of the other (in  
105 Figure 1a this would represent a total of 4 webs and in Figure 1b a total of 2 webs) which again can differ in thickness and/or can consist of different materials. For example a relatively thin and non-tacky web may be used as  
110 the inner web which comes into contact with the polymer, whilst a thicker web may be used as the outer web which is subjected to greater mechanical stressing but in whose case there is not danger of adhesion to the polymer.  
115 Possibilities such as these are also of significance in cases where one web is to be used for example as a packaging material.

By using a double web, it is also possible to employ an inner web consisting of a metallic  
120 material, for example in the form of a metal mesh, thus providing in certain cases for improved dissipation of heat.

The process according to the invention may be used quite generally for the continuous  
125 bulk polymerisation of free-flowing materials, irrespective of type. The process according to the invention is particularly suitable in cases where solid polymers are formed. However, it is intended in particular for the homopoly-  
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merisation and copolymerisation of compounds containing polymerisable oxygen functions such as for example ethers, acetals, ketals and esters. Compounds of this kind include above all those of the kind containing at least one C—O—C bond in cyclic or linear arrangement such as for example cyclic aliphatic or cyclic araliphatic acetals, especially formals or ketals, especially of aliphatic diols or oxadiols, such as 1,3 - dioxolan, 1,3 - dioxacycloheptane, 1,3,6 - trioxa - octane, trioxane, tetroxane, trioxepane; cyclic aliphatic or cyclic araliphatic esters for example lactones; cyclic aliphatic or cyclic araliphatic ethers such as ethylene oxide, epichlorhydrin, other olefin oxides, tetrahydrofuran, styrene oxide or polymeric esters, acetals and ethers such as polydioxolan, polyepoxides and copolymers of trioxane and ethylene oxide. As shown in the last examples above, the compounds to be polymerised may already be in the form of polymers (prepolymers).

The most important application of the invention is in the field of the homopolymerisation or copolymerisation of trioxane or tetroxane. Trioxane or tetroxane can be copolymerised with in particular comonomers or even polymeric compounds of the kind which lead to polyoxymethylenes with oxyalkylene units interspersed in them (alkylene: at least 2 carbon atoms and preferably 2 to 5 carbon atoms), such as for example the aforementioned cyclic acetals, ethers or polymeric acetals and ethers. The starting components can be mixed in any ratio.

However, it is also possible to use other comonomers and polymeric compounds normally used in copolymerisation of trioxane, for example substances with a carbon carbon double bond or triple bond, such as styrene, acrylonitrile and copolymers of methyl methacrylate and styrene. It is also possible to add chain-transfer agents by which stable terminal groups are incorporated. Examples of chain-transfer agents of this kind include aliphatic or araliphatic or aromatic linear ethers (for example dibenzyl ether, diisopropyl ether), acetals, ketals, esters or anhydrides.

In addition to those substances which take part in the polymerisation reaction, it is of course possible for other additives to be present, including plasticisers, stabilisers of various kinds, dyes, pigments, fillers, expanding agents and regulators.

It is also possible using the process according to the invention to further polymerise substances which are themselves polymers (preferably prepolymers of trioxepane) into products of higher molecular weight. In this case however, the prepolymer must be free-flowing or capable of being converted into a free-flowing form at temperatures which are not too high or alternatively it must be soluble in a second free flowing or liquid substance,

generally a monomer. It is also possible to use substances with more than one polymerisable group as the comonomer or even as the prepolymer and in this way to obtain cross-linked products.

The process according to the invention is also particularly suitable for polymerisation reactions that are affected by atmospheric influences (atmospheric moisture, CO<sub>2</sub>, oxygen), such as for example the cationic polymerisation of in particular trioxane and tetroxane.

Polymerisation is initiated by means of initiators, including cationic, anionic or radical initiators or even high-energy radiation. Ionic (cationic or anionic) catalysts are particularly suitable for the polymerisation of oxacyclic compounds or polymeric compounds with C—O—C bonds. Cationic initiators, such as protonic acids; Lewis acids, H-acid acids with complex anions such as for example perchloric acid, and HBF<sub>4</sub>; oxonium salts: perchloric acid esters; and perchloric acid anhydrides, are particularly suitable for use in the case of cyclic ketals and acetals. The process is also particularly suitable in cases where highly active initiators are used, such as perchloric acid or perchloric acid derivatives, also fluorine-containing catalysts, for example antimony pentafluoride and its complexes.

It is best to start with a homogeneous liquid mixture of the reactants which is not prepared until just before introduction into the sheath. The residence time of the completed mixture in the mixing vessel has to be adjusted by regulating the rate at which the individual components are run in and the rate at which the completed homogeneous mixture is run off, in such a way that the mixture is still free flowing or thinly liquid when introduced into the sheath.

In one modification of the process according to the invention, a solution of the catalyst is not mixed with the mixture to be polymerised, instead this solution is sprayed on to the inside of the sheath before the mixture to be polymerised is run in, so that the inner wall of the sheath is as it were impregnated with the finely divided catalyst. Similarly, the catalyst may also be coated on to the inside of the sheath in the form of a solution or paste. In order uniformly to distribute the catalyst in the mixture to be polymerised, the sheath can be passed through several double rollers arranged one behind the other and at the same time intensively kneaded for example immediately after the mixture to be polymerised has been introduced into it.

In some cases, it is possible to obtain an increase in the conversion rate using less active initiators, for example boron trifluoride or derivatives thereof, by subsequent tempering in the sheath, for example at temperatures of from 70 to 80°C.

Conventional expanding agents may be added to the starting mixture to produce foamable polymers.

5 In the process according to the invention, subsequent additions or re-additions (for example of initiator, expanding agent, dye, or gases) are possible providing the contents of the sheath lend themselves to homogeneous admixture.

10 In addition, it is possible to remove residual monomers, and for example formaldehyde, under suction by way of the ends of the edge zones (for example the points denoted by the reference 5 in Figures 1a to 1c or in Figure 4) and if desired to recycle these substances to the starting mixture. For example, it is possible in the case of a polymerisation reaction in which one or more of the starting components partly escape during the reaction, to use an excess of these components at the out-  
20 set so that the components are ultimately present in the required ratio by virtue of the continuous working cycle.

25 To carry out the process according to the invention, the initiator may be added to the material to be polymerised immediately beforehand or continuously, for example by spraying it in with a pump, or by means of a mixer, for example a colloid mill. In cases where prepolymers are used, the initiator still  
30 present from their preparation and, optionally regulators too can be used or replenished. In cases where it is desired to use quick-acting initiator systems, the substance to be polymerised may for example be divided up into two parts and only such constituents of the initiator system added to each of these parts that mixtures that can be stored for sufficiently long periods are obtained. The two  
40 parts are then combined which can be done for example by using two pipes which merge with one another. The material is continuously introduced in this form into the sheath in such quantities that almost all the air is displaced  
45 from the sheath, for which purpose a protective gas may also be used. The rate at which the liquid or free-flowing mixture to be polymerised is introduced is best adapted to the required layer thickness in such a way that the quantity introduced corresponds exactly to the quantity of solid polymer removed. The filled container is then passed either through an air bath or preferably through a liquid bath which has been heated  
50 to the requisite polymerisation temperature. Final polymerisation takes place as the container passes through the bath. The throughput rate is best adapted to the length of the tempering bath or cooling bath in dependence upon the amount of heat of polymerisation liberated. With a tempering bath of given  
55 length, the throughput rate will be reduced for example in the case of excessive heat of reaction or prolonged heat of reaction, and conversely the tempering bath can of course

also be made correspondingly longer. After it has passed through the bath, the container can be taken through a tempering zone. Thereafter, the polymer may either be removed from the unfolded webs and for  
70 example size-reduced. It is also possible to guide the filled sheath through the bath and to shape it in such a way that mouldings in the form for example of panels or profiles are directly obtained. Moulding preferably takes place just before the polymerisation mixture solidifies.

The perchlorate initiators for whose use in addition to others the process according to the invention is particularly suitable, are described in the following. The initiators are based essentially on perchloric acid esters, mainly with aliphatic alcohols, for example  
80 tert. butyl perchlorate, methoxymethyl perchlorate or with aromatic or araliphatic alcohols such as triphenyl methyl perchlorate, methyl diphenyl methylperchlorate, dimethylphenylmethylperchlorate, and on perchloric acid anhydrides, mainly anhydrides of perchloric acid and carboxylic acids such as acetyl perchlorate, benzoyl perchlorate, on ether or ketone perchlorates and on inorganic perchloric acid derivatives of the kind described for example in Gmelin's Handbuch der anorganischen Chemie, 8th edition, system No. 6, pages 391—400 and Supplement [B],  
95 pages 463—65.

Examples of perchlorates such as these include salts of perchloric acid, anhydrides of perchloric acid with inorganic acids, (for  
100 example  $\text{NOClO}_4$ ), organometallic perchlorates (for example trimethyl silylperchlorate, triphenyl stannylperchlorate), iodoniumperchlorate, telluriumperchlorate, antimonylperchlorate and thalliumperchlorate.

105 The invention is further illustrated by the following Examples.

#### EXAMPLE 1

A mixture of 97.3 parts by weight of trioxane containing less than 20 ppm of water, 3.0 parts by weight of 1,3 - dioxolan and 0.22 parts by weight of butylal is continuously delivered at a temperature of approximately 70°C. into a mixing chamber where it is intensively mixed by means of a high speed  
110 stirrer with 0.1 part by weight of a solution of  $\text{HClO}_4$  in the dimethyl ether of ethylene glycol (1 part by weight of 70% aqueous  $\text{HClO}_4$  in 4500 parts by weight of the dimethyl ether of ethylene glycol) and then introduced after a residence time of approximately 2 seconds into a polypropylene sheath folded in accordance with Figure 1b. The delivery rate amounts to 12 litres per minute. The web of polypropylene film used for the sheath (110 cm. wide, 0.2 mm. thick) is unwound from a roll in the form of a double web folded in the middle before the feed zone. The two edges lying one upon the other  
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are bent upwards at right angles by two guide plates (one on the outside, one on the inside) so that the vertically projecting piece of film amounts to approximately 10 cm. (cf. Figure 1b). The film is then guided obliquely downwards into a 3.5 metres long water bath heated to 60°C. so that only the upwardly bent piece of film projects snorkel fashion. The sheath and the polymerising mixture inside it are drawn at a rate of 1 metre per minute over a perforated plate fixedly immersed in water. This perforated plate extends over the entire length of the bath and at one end is bent upwards at right angles and thus forms an outer guide plate for the sheath.

The sheath is kept in the form shown in Figure 1b by spring-mounted rollers arranged at intervals of approximately 20 cm. in the direction of movement on the top side and similar rollers on the side edge (position 4 in Figure 1b). The length of the rollers which are mounted on the upper edge of the sheath, is equal to the width of the sheet (40 cm.).

The guide plates and guide rollers are arranged in such a way that the polymerising mixture receives a cross-section of approximately 3×40 cm. In the first third of the bath, polymerisation has progressed to such an extent that the mixture hazes through crystallising polymer. Any vapours escaping during polymerisation are removed through a slot in a suction means engaging over the "snorkel". After passing through the water bath, polymerisation is substantially over and the crude polymer is cooled in a following cold water bath 6.5 metres long. The sheath is then opened and rolled up whilst the crude polymer is laterally discharged, dropping into a crusher and then into a mill. The size-reduced crude polymer is boiled for 1 hour with 0.1% of ammonium carbonate solution in order to destroy the catalyst and to remove the unreacted monomer. A copolymer with a reduced viscosity  $\eta_{red}=0.63$  (100 ml/g, dimethyl formamide solution, 135°C.) coupled with outstanding thermal stability is obtained for an 82% conversion. The weight loss following 2 hours' heating under nitrogen to 220°C. only amounts to 2.8%. Thermal stability can be even further improved by conventional means, for example by hydrolytic degradation of the chain ends and by adding stabilisers. It is possible in this way to obtain a product of outstanding thermal stability which is particularly suitable for use in the manufacture of injection mouldings. It is of course possible by reducing the regulator component, in this example the quantity of butylal, to obtain copolymers of considerably higher molecular weight which can be used for example both for extrusion and for blow-mouldings.

The guide means in the cooling bath can also be designed in accordance with Figures 5 and 6. The perforated plate upon which the

sheath containing the polymerisation mixture lies is denoted by the reference 13. The layer thickness of the mixture is adjusted by rollers 20. These rollers are secured to spring-mounted stirrups 22 which are in turn secured to supports 21 which can be screwed for example to the edge of the trough. The supports 21, the stirrups 22 and the rollers 20 are removable so that the rollers can be adjusted at any distance apart from one another. In general, the rollers will be mounted at shorter intervals apart during the initial phase of polymerisation than later on when the polymerisation mixture is more solid or even completely solidified. Figure 6 shows the arrangement illustrated in Figure 5 in the longitudinal direction, the various intervals between the supports 21 being shown particularly clearly.

## EXAMPLE 2

A mixture of 180 parts by weight of trioxane containing less than 20 ppm of water, 7.2 parts by weight of 1,3 - dioxepane and 0.2 part by weight of methylal is continuously pumped at a temperature of 75 to 80°C., into a mixing chamber where it is intensively stirred by means of a high speed stirrer with one part by weight of a  $\text{BF}_3$  solution (consisting of 1 part by weight of  $\text{BF}_3$ , 8.8 parts by weight of dibutyl ether and 496 parts by weight of 1,2 - dichloroethane) and then, after a residence time of approximately 2 seconds, is delivered as shown in Figure 7 through a feed pipe 15 between two endless webs 1 and 2 of glass-fibre-reinforced polytetrafluoroethylene 35 cm. wide and 0.35 mm. thick whose edge zones 5 have been bent upwards together. The delivery rate amounts to 8 litres per minute. The two edges of the lower part of web 1 (1') and of the upper part of web 2 (2') are bent upwards by means of transversely mounted rollers 20 (profile) and laterally arranged guide plates so that the two webs assume the form of a trough 9 open at both ends whose profile is shown in Figure 8. This trough 9 is open in the longitudinal direction, in other words the two transverse walls are missing, and is 1 metre long. The webs 1 and 2 bent upwards along their edges are then introduced obliquely downwards into the trough. During the initial stages of the process, a sealing element, for example in the form of a suitable piece of sponge rubber wrapped in polyethylene film, is placed between the webs so that the required level can be built up. This piece of sponge rubber which seals off the mould formed by the webs towards the front, is best inserted where the webs run into the trough and more particularly where the first trough guide roller (see below) is mounted. There is no need for a complete seal towards the front because the mixture thickens after 10 to 20 seconds. The lower web 2 sinks into the trough 9 under the weight-

of polymerising mixture 7. The upper band 1 is pressed down by means of the guide rollers to such a depth that it comes into contact with the surface of the still liquid mixture (see Figure 8). In this way, polymerisation is able to proceed in the absence of any interference from atmospheric influence, and evaporation is reduced. Evaporation can be further reduced by cooling the upper web for example with water. However, it is not absolutely necessary to cool the web or to provide a separate temperature bath for absorbing the heat of polymerisation. As shown in Figure 8, it is sufficient for example for the sheath to be merely surrounded by the ambient air during the polymerisation reaction. The polymerising mixture 7 (Figure 8) receives a cross-section with an average length of approximately 20 cm. and a width of 4 cm. through the shape of the webs and their distance apart from one another and by the adjustment of the throughput rate and take off rate.

After passing through the trough, the webs together with their now solid contents are drawn over rollers 25 (Fig. 7), the upwardly bent edges being converted back into the horizontal by means of laterally arranged side plates. The bands are guided over deflecting rollers 23 and finally removed through the take-off rollers 24. Any residues of monomers or polymers adhering to the webs are removed by scrapers or brushes. The useful length of the installation amounts for example to 6 metres, and the take off rate to 1 metre per minute.

If a chain conveyor open at both ends (front and rear) is used instead of a trough line and part of the rollers (7), its links being in the form of the trough, it is possible to reduce the tensile load on the polytetrafluoroethylene web and the wear due to friction occurring over prolonged periods of operation.

The polymer drops through chute 26 into collecting baskets (not shown) and, to complete the conversion, is tempered for some 15 minutes at 80°C. before size-reduction. It is worked up as described in Example 1. A copolymer with a reduced viscosity  $\eta_{red}=0.61$  is obtained for an 80.5% conversion, its weight loss after 2 hours' heating under nitrogen to 220°C. amounting to 2.1%.

#### WHAT WE CLAIM IS:—

1. A process for the production of a homo or copolymer by continuous bulk polymerisation in the presence of a polymerisation initiator in which a polymerisation mixture is continuously introduced by means of at least one feed unit in at least one feed zone into a constantly moving sheath, after substantially all the air has been displaced from the sheath, the sheath being formed of a flexible material which lies loosely in the vicinity of the feed zone, and the sheath is

thereafter guided through a zone heated to the polymerisation temperature, the sheath being formed continuously from two separate webs of the flexible material which are guided together in the vicinity of the feed unit so that they lie loosely one on top of the other with the feed unit in between them, or from a single web of the flexible material which is folded along one line or along two lines in the vicinity of the feed unit so that two portions of the web lying loosely one on top of the other are formed with the feed unit in between them, and after passing the feed unit, but before reaching the zone heated to the polymerisation temperature, the open longitudinally extending edge zones of the web(s) lying one on top of the other are brought together and bent upwards by guide means to form the sheath acting as a liquid-tight polymerisation vessel, in such a way that the sheath either takes the form of two troughs inserted one inside the other, the polymerisation mixture filling the bottom of the lower trough whilst the side walls of both troughs run parallel to one another above the polymerisation mixture and are bent upwards, or takes the form of a slit tubular structure with parallel edges, the edge(s) of the tubular structure which extend beyond the polymerisation mixture being bent upwards.

2. A process as claimed in claim 1 wherein the sheath is subsequently guided through a cooling bath.

3. A process as claimed in claim 1 or 2, wherein after introduction of the polymerisable mixture the sheath is formed so as to give it U- L- or inverted-T-profile.

4. A process as claimed in any of claims 1 to 3, wherein the sheath follows a downwardly sloping course after the first feed zone, a horizontal course during polymerisation and an upwardly inclined course on completion of polymerisation.

5. A process as claimed in any of claims 1 to 4, wherein the polymerisation mixture to be polymerised contains cyclic compounds with at least one C—O—C bond in the ring or linear polymeric compounds with C—O—C bonds.

6. A process as claimed in claim 5, wherein the polymerisation mixture contains one or more cyclic acetals and/or linear polyacetals.

7. A process as claimed in any of claims 1 to 6, wherein the polymerisation mixture contains trioxane or tetroxane.

8. A process as claimed in any of claims 1 to 7, wherein the polymerisation mixture contains a cationic initiator.

9. A process as claimed in claim 8, wherein the initiator is perchloric acid and/or a perchloric acid ester and/or a perchloric acid anhydride.

10. A continuous bulk polymerisation process substantially as hereinbefore described



with reference to any of the accompanying drawings and/or the examples.

5 11. A polymer or co-polymer when produced by a process as claimed in any of claims 1 to 10.

10 12. An apparatus for carrying out a bulk polymerisation process comprising means for forming one or two webs of flexible material into a continuously moving sheath, feed means for introducing a polymerisation mixture into the sheath, a zone capable of being heated to the polymerisation temperature and means for guiding the sheath therethrough, the forming and guiding means either being  
15 adapted to form after insertion of the polymerisation mixture by the feed means a single web into a slit tubular structure with parallel edges, the edges of the slit being bent upwards, or two webs into two troughs  
20 inserted one inside the other, the edges of which are brought together and bent upwards.

13. An apparatus as claimed in claim 12 including means for discharging polymer formed from the sheath.

14. An apparatus as claimed in claim 12 25 or 13 wherein the heatable polymerisation zone is a liquid bath.

15. An apparatus as claimed in any of claims 12 to 14, wherein the forming and guiding means are adapted so that the sheath 30 follows a downwardly sloping course after passing the feed means, a horizontal course whilst passing through a heatable polymerisation zone and an upwardly inclined course thereafter.

16. An apparatus for carrying out a bulk polymerisation process substantially as hereinbefore described with reference to any of the figures of the accompanying drawings. 35

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COMPLETE SPECIFICATION

4 SHEETS

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Sheet 1

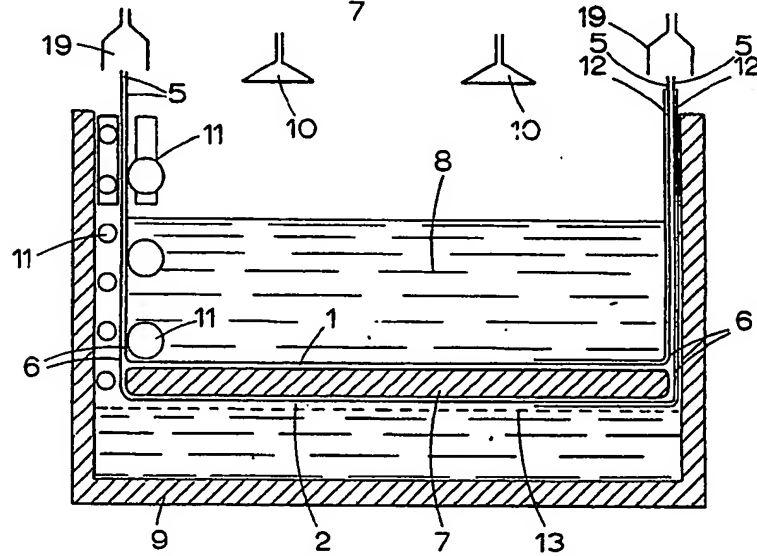
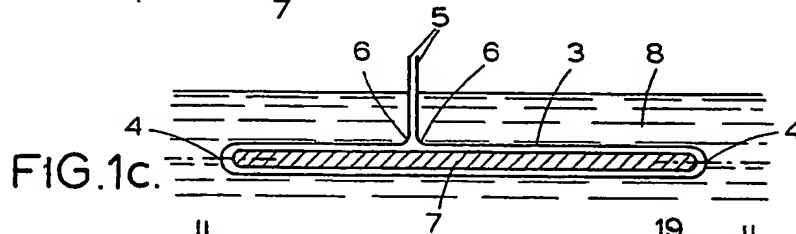
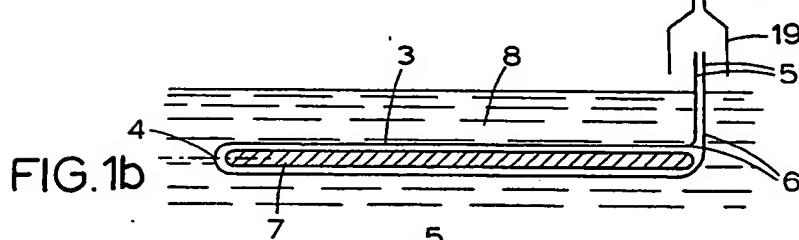
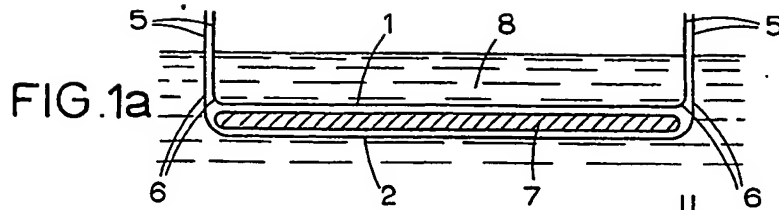


FIG. 2.

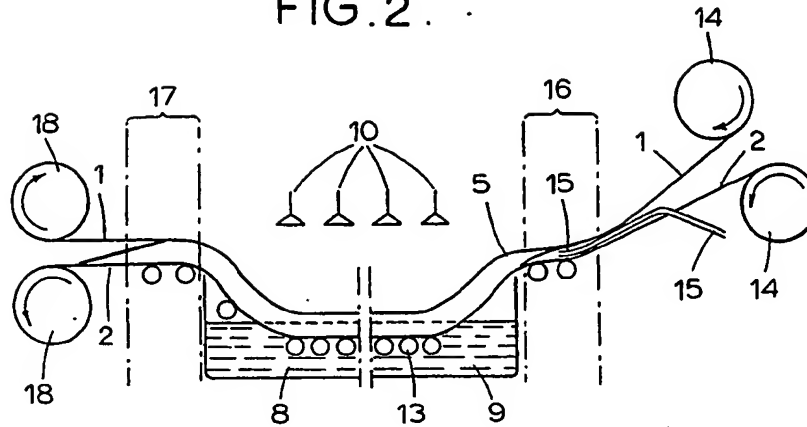


FIG. 3.

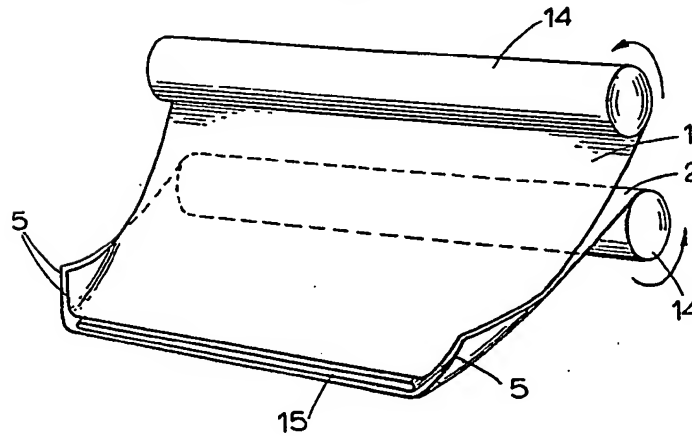


FIG. 5.

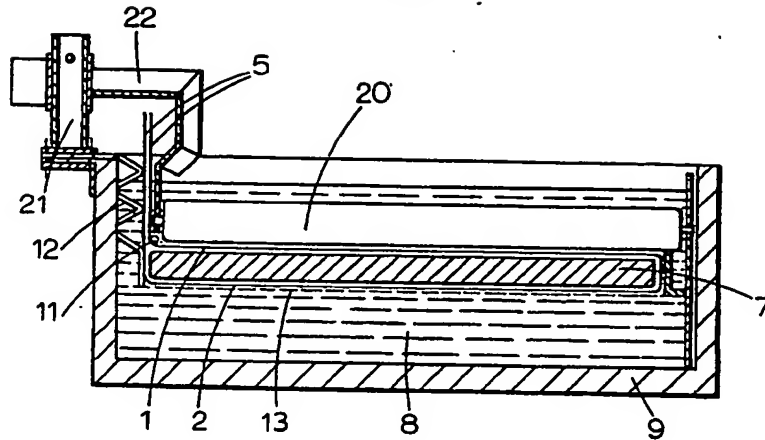
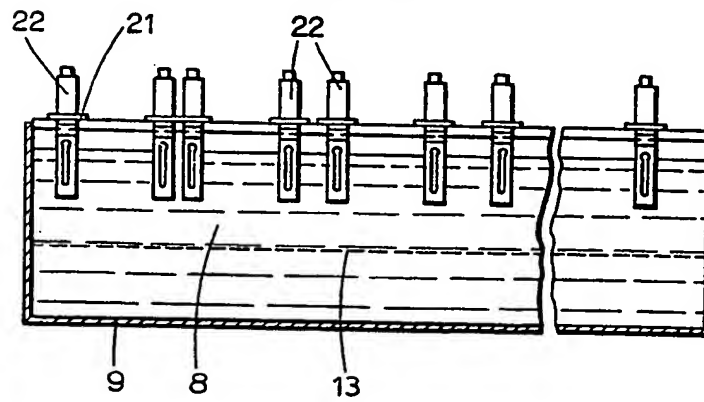


FIG. 6.



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Sheet 4

FIG. 7.

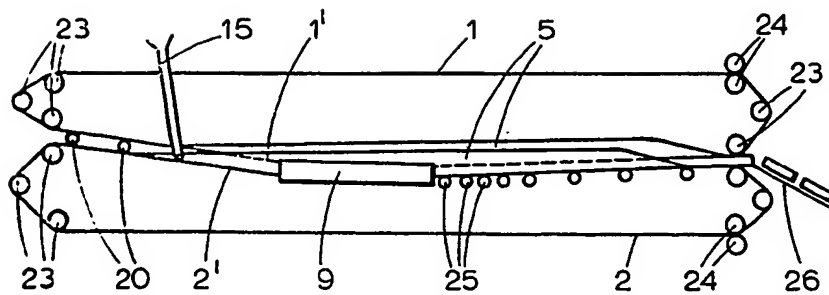


FIG. 8.

